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Version of attached file:

Published Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

González-Martínez, M. L. and Hutson, J. M. (2013) 'Ultracold hydrogen atoms : a versatile coolant to produce ultracold molecules.', *Physical review letters.*, 111 (20). p. 203004.

Further information on publisher's website:

<http://dx.doi.org/10.1103/PhysRevLett.111.203004>

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Ultracold Hydrogen Atoms: A Versatile Coolant to Produce Ultracold Molecules

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(Received 27 May 2013; published 12 November 2013)

We show theoretically that ultracold hydrogen atoms have very favorable properties for sympathetic cooling of molecules to microkelvin temperatures. We calculate the potential energy surfaces for spin-polarized interactions of H atoms with the prototype molecules $\text{NH}(^3\Sigma^-)$ and $\text{OH}(^2\Pi)$ and show that they are shallow (50 to 80 cm^{-1}) and only weakly anisotropic. We carry out quantum collision calculations on $\text{H} + \text{NH}$ and $\text{H} + \text{OH}$ and show that the ratio of elastic to inelastic cross sections is high enough to allow sympathetic cooling from temperatures well over 1 K for NH and around 250 mK for OH.

DOI: [10.1103/PhysRevLett.111.203004](https://doi.org/10.1103/PhysRevLett.111.203004)

PACS numbers: 37.10.Mn, 34.50.Cx, 37.10.Pq

Samples of ultracold molecules, at temperatures below 1 mK, have potential applications in fields ranging from high-precision measurement to quantum simulation [1]. Ultracold polar molecules are particularly interesting because they have long-range anisotropic interactions whose strength can be tuned with applied electric field, which are important in understanding the properties of dipolar quantum gases.

There have been great advances in producing ultracold molecules in the last few years. Many groups have succeeded in producing alkali-metal dimers in high-lying vibrational states by either magnetoassociation or photoassociation [2–4], and a small number of such species have been transferred to their absolute ground states, either incoherently by absorption followed by spontaneous emission [5,6] or coherently by stimulated Raman adiabatic passage (STIRAP) [7–10]. KRB molecules produced by STIRAP [8] have been used to investigate ultracold chemical reactions [11,12] and the properties of dipolar quantum gases [12].

The indirect methods that produce ultracold molecules via ultracold atoms are inherently limited to molecules formed from atoms that can themselves be cooled. So far this has restricted molecule formation experiments to the alkali-metal dimers, although there are prospects for extending the approach to a wider range of species, such as $^2\Sigma$ molecules formed from an alkali-metal atom and an alkaline-earth [13] or Yb [14,15] atom. However, there is also great interest in producing ultracold samples of a wider range of species, including polyatomic molecules such as ND_3 [16] and CH_3F [17] and reactive species such as NH [18–22] and OH [23–29]. Methods such as buffer-gas cooling [30], molecular beam deceleration [16], and velocity filtering [31] have been developed, which are capable of producing trapped samples at temperatures between 10 and 500 mK, but the ultracold regime (below 1 mK) has not yet been reached.

There is thus a great need for a second-stage cooling method that can cool molecules from tens or hundreds of

millikelvin to the ultracold regime. The principal candidates are laser cooling, evaporative cooling, and sympathetic cooling. Laser cooling was for a long time dismissed as a method of cooling molecules, because electronically excited molecules can in principle reradiate to many different vibrational levels of the electronic ground state. However, in the last few years considerable progress towards laser cooling has been made for molecules with unusually good overlap between the ground and excited vibronic states [32,33], and Hummon *et al.* [34] have succeeded in producing a magneto-optical trap for YO molecules. Nevertheless, laser cooling is likely to remain applicable to only a very restricted set of molecules.

Sympathetic cooling relies on the thermalization of the “warm” species of interest by collisions with ultracold atoms. It has been widely used to cool molecular ions (for a recent compilation, see Ref. [35]) and neutral atoms [36,37]. Its use for neutral molecules was proposed by Soldán and Hutson [38] in 2004, but it has not yet been experimentally demonstrated. The difficulty is that static electric and magnetic traps can confine molecules only when they are in low-field-seeking states, and these states are never the lowest state in the applied field [39]. Collisions that transfer molecules to the lower states release kinetic energy and eject both the atoms and the molecules from the trap. The key quantity that determines the feasibility of sympathetic cooling is the ratio γ between the cross section for elastic collisions (which produce thermalization) and that for inelastic collisions (which cause trap loss). A common rule of thumb is that, for cooling to be successful, this ratio needs to be at least 100 [41].

There has been a long search for atom-molecule pairs that would be good for sympathetic cooling. However, extensive theoretical work [42–46] and some experimental work [46] has shown that, for most experimentally accessible combinations of atoms and molecules, inelastic collisions will lead to unworkable trap losses. Inelastic cross sections can be suppressed at low collision energies by

centrifugal barriers that exist for the collision products [42–44,47,48], but even for light atoms such as lithium the barriers are only around 3 to 12 mK high [44], and strong inelasticity sets in for collisions above this energy. The best system proposed so far is Mg + NH [42,43], where sympathetic cooling is predicted to succeed if the molecules can be precooled to 10–20 mK. Unfortunately, such temperatures can so far be achieved only for very small numbers of molecules.

The purpose of the present Letter is to propose ultracold atomic hydrogen as a versatile sympathetic coolant for molecules. Magnetically trapped hydrogen atoms have been produced at temperatures of 40 to 100 mK and densities up to $3 \times 10^{14} \text{ cm}^{-3}$ by purely cryogenic methods [49,50], and then evaporatively cooled to produce a Bose-Einstein condensate (BEC) of 10^9 atoms at a temperature around 50 μK and densities between 10^{14} and $5 \times 10^{15} \text{ cm}^{-3}$ [51]. For sympathetic cooling purposes BEC is unnecessary, but the large densities and cloud sizes achievable are very valuable. Furthermore, because of the low mass and small polarizability of atomic hydrogen, the centrifugal barriers for collisions with molecules such as NH and OH are around 400 mK high. As will be seen below, this produces very favorable conditions for sympathetic cooling, starting from temperatures of 250 mK for OH and over 1 K for NH. This is a crucial improvement over earlier proposals, because very large numbers of cold molecules can be produced at these higher temperatures.

We consider $\text{NH}(^3\Sigma^-)$ and $\text{OH}(^2\Pi)$ as prototype molecules. NH molecules have been cooled by buffer-gas cooling [19] and trapped at a peak density of 10^8 cm^{-3} and a temperature of a few hundred millikelvin [20]. NH has also been decelerated [52] and trapped electrostatically [21] in its $a^1\Delta$ state and subsequently pumped into the $^3\Sigma^-$ state [22], allowing accumulation in a magnetic trap. $\text{OH}(^2\Pi)$ has also been decelerated electrostatically [23–25,53] and trapped both electrostatically [23] and magnetically [26,54], and Stuhl *et al.* [29] have very recently achieved evaporative cooling to a temperature around 5 mK.

We have calculated the potential energy surfaces for interaction of ground-state $\text{NH}(^3\Sigma^-)$ and $\text{OH}(^2\Pi)$ molecules with H atoms. For NH there are two surfaces, of $^2A''$ and $^4A''$ symmetry, whereas for OH the H atom splits the degeneracy of the Π state to produce four surfaces, of $^1A'$, $^1A''$, $^3A'$, and $^3A''$ symmetry. Our primary interest is in collisions of atoms and molecules in spin-stretched states, in which all the quantum numbers for the projections of angular momenta onto the magnetic field direction have their maximum values. Such collisions occur principally on the *high-spin* potential surfaces. By contrast with systems like $\text{NH} + \text{NH}$ [55], there are no exothermic reaction channels on the low-spin surfaces. We have calculated the high-spin surfaces using an open-shell restricted version of the coupled-cluster method with single, double, and non-iterative triple excitations, RCCSD(T), as implemented in MOLPRO [56]. Correlation-consistent aug-cc-pVQZ basis sets [57] were used, with *spdf* functions for H and *spdfg* functions for N and O. The basis sets also included *spdf* bond functions halfway between the molecule and the H atom, as in Ref. [58]. All interaction energies were corrected for basis-set superposition error using the counterpoise correction [59]. The resulting surfaces are shown in Fig. 1, and it may be seen that they are fairly weakly anisotropic, with well depths between 60 and 80 cm^{-1} and anisotropies of tens of cm^{-1} . This may be contrasted with the interaction potentials with alkali-metal atoms, which for NH have anisotropies ranging from 500 to 1700 cm^{-1} [58]. The NH and OH bond lengths were fixed at the equilibrium for the free molecules, $1.95770 a_0$ and $1.83417 a_0$. This prevents exothermic reactions to form $\text{N}(^4\text{S}) + \text{H}_2$ or $\text{O}(^3\text{P}) + \text{H}_2$, but in each case there is a substantial barrier to reaction (1000 K for NH [60] and 5200 K for OH [61]) that is likely to suppress reactive processes in the ultracold regime.

To evaluate the feasibility of sympathetic cooling, we need to calculate the ratio γ of elastic to inelastic cross sections as a function of collision energy E and magnetic field B . As a first step, we carried out coupled-channel calculations

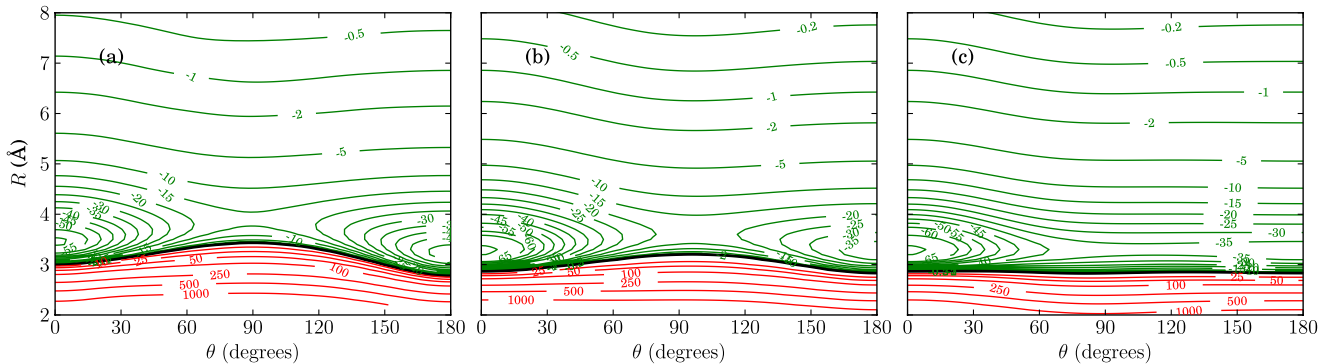


FIG. 1 (color online). *Ab initio* interaction potentials for (a) the $^4A''$ high-spin state of $\text{H} + \text{NH}$, (b) and (c) the $^3A'$ and $^3A''$ high-spin states of $\text{H} + \text{OH}$, respectively. Contours are labeled in units of cm^{-1} , with 180° corresponding to the H atom approaching the molecule from the hydrogen side.

of $\text{H} + \text{NH}(^3\Sigma^-)$ and $\text{H} + \text{OH}(^2\Pi_{3/2})$ collisions, neglecting hyperfine interactions, using the MOLSCAT program [62] with computational methods identical to those in previous work on $\text{N} + \text{NH}$ [63] and $\text{N} + \text{OH}$ [64] collisions. The methods used are described briefly in the Supplemental Material [65].

The energy levels of H , NH , and OH are shown as a function of magnetic field B in Fig. 2. We have calculated elastic and total inelastic cross sections for atoms and molecules initially in the magnetically trappable states shown as dashed blue lines. Inelastic collisions that change the state of either the atom or the molecule are fully included, but those that change the molecular state dominate. Incoming partial waves up to $L = 2$ are included to give convergence of cross sections up to collision energies of about 4 K; the $L = 3$ centrifugal barriers are about 6 K high. These calculations set the low-spin (singlet or doublet) surfaces to be the same as the corresponding high-spin (triplet or quartet) ones. This latter approximation is reasonable because states with different total spin S are coupled only by weak monomer fine-structure and hyperfine terms.

The ratio γ is shown as a contour plot in Fig. 3(a), for $\text{H} + \text{NH}(^3\Sigma^-)$. The solid black line shows the maximum magnetic field sampled in a quadrupole trap with an energy of $6k_B T$, chosen so that 99.9% of molecules sample fields below the line. It may be seen that γ remains above 10^4 for almost all energies and fields below the line at temperatures up to well above 1 K, except for a fairly narrow band around 1 K where γ decreases to about 100; this is due to a d -wave resonance in the incoming channel. The results in Fig. 3(a) suggest that sympathetic cooling can succeed for NH molecules starting from remarkably high initial temperatures: even the resonance near 1 K can probably be crossed in a few collisions with relatively little loss of molecules from the trap.

We have investigated the robustness of this result to the approximations made in Fig. 3(a). First, we have investigated the effect of scaling the potential energy surface by $\pm 5\%$ from the one shown in Fig. 1(a). The resonance around 1 K shifts by about ∓ 0.2 K over this range but the value of γ close to the resonance does not change

significantly. The dependence on the potential is far weaker for collisions with H atoms than for collisions with heavier atoms and deeper interaction potentials [42,44,66]. Secondly, we have investigated the effect of introducing a deeper well for the $^2A''$ state. The true doublet surface is around $35,000 \text{ cm}^{-1}$ deep, and we cannot converge our calculations with such a deep well, but we have explored the effects of introducing an approximate $^2A''$ surface given by $V_{2A''} = \lambda_2 V_{4A''}$ ($1 < \lambda_2 \leq 1.25$). Additional resonances occur for some values of λ_2 , but we did not observe the ratio γ dropping below 200 in any of the cases we investigated. Finally, we have investigated the effect of including the hyperfine interactions for both ^1H and ^{14}NH , using a generalization of the methods developed in Ref. [43] to include the atomic hyperfine term. These calculations are too expensive to produce a full contour plot, but we find that the main effects are the same as observed for $\text{Mg} + \text{NH}$ [43]: the existence of energy splittings that persist at zero field [see solid lines in Fig. 2(a) and inset of Fig. 2(b)] makes the kinetic energy release almost independent of field below about 100 G for collisions that change the atomic hyperfine state. The total inelastic cross sections are almost independent of field and proportional to $E^{-1/2}$ in this region, while the elastic cross sections are essentially constant. The ratio γ is thus proportional to $E^{1/2}$. For NH initially in its spin-stretched state with total spin projection $m_f = +5/2$, γ remains above 2300 at collision energies above $50 \mu\text{K}$. Our overall conclusion from all these tests is that none of the approximations made in Fig. 3(a) will qualitatively affect the success of sympathetic cooling.

For $\text{H} + \text{OH}$ the situation is a little more complex. $\text{OH}(^2\Pi)$ exhibits Λ -doubling, which splits its lowest rotational state $j = 3/2$, $\omega = 3/2$ into e and f components, with the f state lying about 0.056 cm^{-1} above the e state at zero electric field, as shown in Fig. 2(c). The state that can be decelerated and trapped electrostatically correlates with the f component, but molecules in either the e or the f state may be trapped magnetically in the $m_j = +3/2$ sublevel. H atoms must be trapped magnetically, so we have carried out coupled-channel calculations for collisions of $\text{H}(m_s = +\frac{1}{2})$

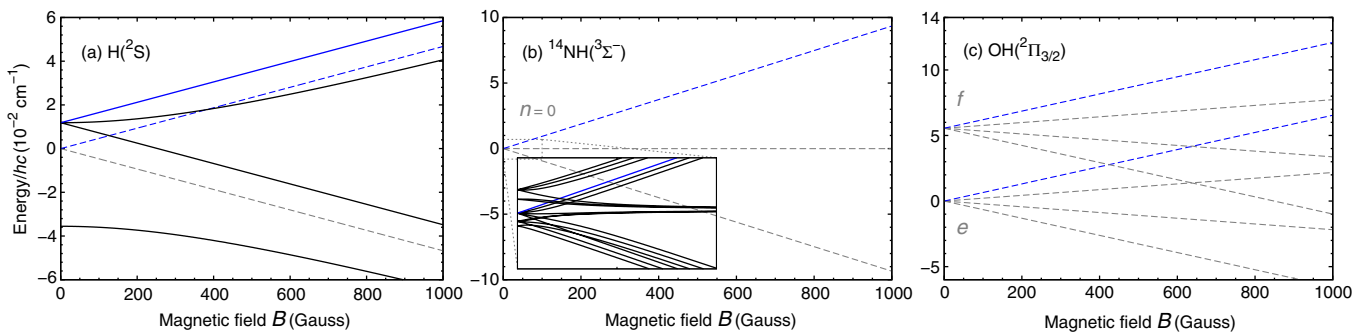


FIG. 2 (color online). Magnetic-field dependence of the energy levels for (a) $\text{H}(^2\text{S})$, (b) $^{14}\text{NH}(^3\Sigma^-)$, and (c) $\text{OH}(^2\Pi_{3/2})$. Solid (dashed) lines correspond to the inclusion (exclusion) of hyperfine terms. The magnetically trappable states for which scattering calculations were carried out are shown in blue (dark gray).

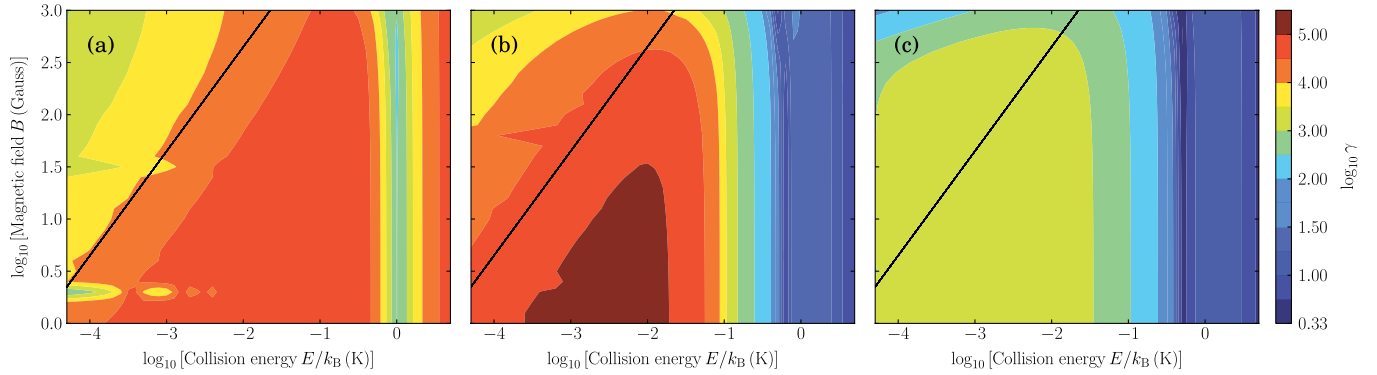


FIG. 3 (color online). Contour plots of the ratio γ of elastic to inelastic cross sections as a function of collision energy and magnetic field. The panels correspond to collisions of spin-polarized hydrogen with (a) NH, (b) OH(*e*), and (c) OH(*f*). The initial states are shown as dashed blue (dark gray) lines in Fig. 2.

with OH in the $m_j = +3/2$ sublevel of both the *e* and *f* states. The resulting contour plots of the ratio γ are shown in Figs. 3(b) and 3(c). It may be seen that the results for the *e* state are again very suitable for sympathetic cooling, with $\gamma > 10^4$ for energetically accessible fields at temperatures up to around 100 mK. γ remains above 100 for temperatures up to about 500 mK. The larger inelastic cross sections compared to H + NH reflect the fact that, for $j = 3/2$, the interaction potential can drive spin-changing collisions directly, while for NH($^3\Sigma^-, n = 0$) a higher-order mechanism is involved [67]. For H + OH(*f*), γ does not become as large at low fields, because of the possibility of relaxation to produce OH(*e*) with a kinetic energy release around $80 \text{ mK} \times k_B$, but nevertheless remains above 100 for all accessible fields at temperatures up to about 250 mK. This contrasts with the situation for collisions of magnetically trapped OH(*f*) with other atoms [64,68], even He [69], where the kinetic energy release overcomes the centrifugal barrier and inelastic collisions are too fast for cooling.

Ultracold H atoms have in the past been produced inside a cryogenic environment. It is likely to be quite difficult to introduce a molecular sample into such an environment. An alternative that appears preferable is to extract the hydrogen cloud from the cryogenic environment before evaporative cooling. Alternatively, developments in laser technology may in the future allow Doppler cooling of H atoms. In either case, the most obvious experiments are either to make a separate molecular cloud and bring it into coincidence with the atomic cloud, as has been done for Rb + ND₃ [46], or to decelerate molecules almost to rest at the location of the atomic cloud. Our calculations give elastic cross sections σ_{el} for NH and OH colliding with H atoms in the range 200 to 400 Å²; the H + NH *s*-wave cross section varies by only $\pm 10\%$ when the interaction potential is scaled by $\pm 5\%$. For $\sigma_{\text{el}} = 400 \text{ Å}^2$ and an H-atom sample initially at $T = 50 \text{ μK}$ and density $n_{\text{H}} = 3 \times 10^{14} \text{ cm}^{-3}$, we estimate that cooling from 1 K to 100 μK will take 80 to 90 collisions and be achieved in about 5 s, which is within the lifetime of the atomic cloud.

The very large densities and cloud sizes available for H atoms offer another intriguing possibility. For the densities and cross sections above, the mean free path $(n_{\text{H}}\sigma_{\text{el}})^{-1}$ for atom-molecule collisions is around 1 mm. Higher H atom densities may be achievable, and other molecules may well have larger cross sections. It may therefore be possible to direct a low-energy beam directly onto an atomic cloud, without a final deceleration stage to bring it to rest, and to rely on collisions with H atoms to remove enough kinetic energy for the molecules to be trapped.

In conclusion, we propose that ultracold hydrogen atoms are an extremely promising medium to achieve sympathetic cooling of a wide range of molecules. Because of the large centrifugal barriers in collisions with H atoms, inelastic collisions are substantially suppressed at collision energies below 200 mK, or in some cases much higher.

The authors are grateful to EPSRC for funding and to Tim Softley and Jook Walraven for valuable discussions about the experimental possibilities.

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